Role of the Ligand and of the Size and Flexibility of the Palladium−Ancillary Ligand Cycle on the Reactivity of Substituted Alkynes toward Palladium(0) Complexes Bearing Potentially Terdentate Nitrogen−Sulfur−Nitrogen or Nitrogen−Nitrogen−Nitrogen Ligands: Kinetic and Structural Study

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The reaction between palladium(0) complexes bearing potentially terdentate ligands and dimethyl acetylenedicarboxylate (DMA) to give the corresponding palladacyclopentadiene complexes was studied under kinetic conditions. The reactivity of the complexes was markedly influenced by the nature of the ancillary ligand. Thus, when pyridyldithioether (SNS) and dipyridylthioether (NSN) ligands are used, the reactivity and the rate law of the corresponding derivatives are similar to those of the unsubstituted bidentate pyridylthioether substrates and, therefore, a marked rate increase can be obtained only by reduction of the olefin steric requirement. When terdentate NNN ligands are used, an apparent difference in reactivity between the derivatives bearing the pyridine−amine−pyridine and pyridine−amine−quinoline ligands is observed. On the basis of a detailed structural study (NMR, X-ray) and on kinetic investigations, an interpretation which takes into account the flexibility of the cycle formed between the ligand and palladium is proposed. Thus, irrespective of the size of the cycle, the complexes in which the ligand forms flexible cycles undergo ring opening less easily, with a consequent reduction of reactivity. Conversely, rigid rings cannot undergo associative attack without companion ring opening, this phenomenon being crucial in favoring the alkyne attack.

Introduction

Owing to its importance in several applications in organic synthesis, the chemistry of group 10 metallacycles has been recently reviewed.[1] In particular, palladium metallacycle complexes have been recognized as key intermediates in the synthesis of conjugated dienes[2] and in annulation reactions.[3] We have recently published a detailed study dealing with the kinetics and mechanism of the oxidative addition of activated alkynes on palladium(0) olefin substrates bearing bidentate pyridylthioether ligands to give the corresponding palladacyclopentadienyl derivatives.[4] This kinetic study represents an attempt at filling the gap in the knowledge of the intimate mechanism governing these important reactions which had not been studied before. The mechanism leading to the cyclopalladated product was described by two consecutive steps, in which the first reaction leads to the monoalkyne intermediate which is normally highly reactive and rapidly reverts to the reagents or gives the cyclopalladated product (Scheme 1).

Under the steady-state approximation for the monoalkyne derivative, the rate law becomes

$$\text{rate} = k_2[\text{alkyne}][\text{complex}]$$

where k_2 represents the second-order rate constant related to the alkyne direct attack at the Pd(0) olefin complex. The scheme reported above was generally adopted for almost all the reactions studied, apart from the case in which the bulky 2-((*tert*-butylthio)methyl)-6-methylpyridine (MeN−S*t*Bu) was used as ancillary ligand. In that case an accumulation of the monoalkyne derivative was observed, irrespective of the leaving olefin (tmetc = tetramethyl ethylenetetracarboxylate, ma = maleic anhydride); this behavior was not unexpected, since the stabilization of monoalkyne derivatives due to the enhanced steric demand of the ancillary ligand had already been noted.[5] As a side result, it was possible to determine in the case of the complex [Pd(η^2-ma)(MeN−S*t*Bu)] the equilibrium constant related to the exchange reaction between the leaving olefin, ma, and the entering dimethyl acetylenedicarboxylate (DMA); its value (K_E = 0.014) indicates a more pronounced ability of the olefin with respect to the alkyne to stabilize the palladium(0) derivatives.[4]

It was also noted that in the cases in which no hindered ancillary ligands were employed and with ma as the leaving

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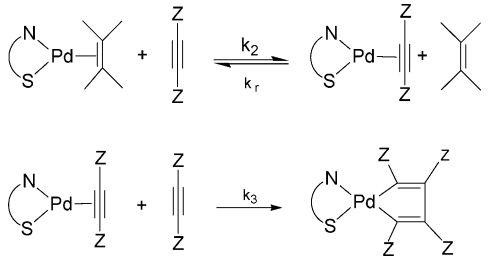
Scheme 1



olefin, two consecutive reactions were observed. Unfortunately, the related rate constants were not accessible, owing to the low absorbance changes coupled with the high reaction rates. For the sake of completeness and in order to explore all the possible ways toward comprehension of the system, we decided to extend our study to the behavior of the olefin derivatives bearing potentially terdentate ligands, in the awareness that they can impart to their derivatives a peculiar reactivity which might complete our knowledge of the intimate mechanism governing the formation of the palladacyclopentadiene species. In this respect we have already observed the interesting chemistry of complexes of the type [Pd(η^2-olefin)(LL′L)] (LL′L = pyridylthioether terdentate ligands) in the reactions of olefin exchange.[6] The terdentate ligand, in fact, usually coordinates to give a bidentate complex, but the metal center undergoes a chelating effect caused by the nucleophile on the dangling uncoordinated ligand arm. Thus, a remarkable fluxionality affects the complexes, which rearrange in solution even at low temperature, and the olefin exchange reactions are characterized by a dissociative path induced by the third dangling coordinating atom.

The ligands, the complexes studied in the present paper, and the adopted numbering scheme are reported in Chart 1.

Results and Discussion

Synthesis of Ligands and Complexes. The new ligands NNNtos(Qui) and NNNtos(Py) were prepared in high yield by coupling 2-picolyl chloride hydrochloride with sodium *N*-tosyl-8-quinolinamide or sodium *N*-2-pyridylmethyltosylamide, respectively, in dimethylformamide (DMF) in the presence of triethylamine (TEA). All other ligands were prepared according to published procedures.

The complexes under study were obtained by addition of the appropriate ancillary ligand and olefin to a solution of $Pd_2DBA_3 \cdot CHCl_3$ in anhydrous acetone under an inert atmosphere (Ar). The palladium(0) complexes bearing NSN(Py) and SNS(Ph) as ancillary ligands have already been described,[6] whereas the NSN(Qui), NNNtos(Py), and NNNtos(Qui) derivatives were not hitherto synthesized and characterized. Only the solution behavior and rearrangements of the latter will be discussed, therefore. The synthesis of palladacyclopentadienyl derivatives can be achieved either from the reaction of palladium(0) monoalkyne complexes with DMA or from the reaction of polymeric $[PdC_4(COOMe)_4]_n$[7] with the appropriate ancillary ligand in anhydrous acetone.[4] Although we have chosen the former method for mechanistic purposes, we have preferred the latter procedure, since it provides for an easy access to a large variety of species under preparative conditions.

Solution Behavior of Pd(0) Olefin Complexes. The synthesis of the complexes [Pd(η^2-ol)(LL′L)] (LL′L = NSN(Qui), NNNtos(Qui), NNNtos(Py); ol = tmetc, Nq) was monitored by means of ^{1}H and ^{13}C NMR, since an upfield and a downfield shift of the signals of the olefin and of the ancillary ligands, respectively, are observed upon coordination. As can be seen from the structures reported in Figure 1, the central aliphatic amine cannot compete with the aromatic pyridine and quinoline. It is well-known, in fact, that the palladium(0) olefin derivatives bearing aliphatic amines are very elusive species.[8,9] From the structures and the topological representation in Chart 2, it can be seen that the palladium(0) derivatives bearing the symmetrical olefin tmetc would give rise to only one isomer. The low-temperature ^{1}H NMR spectra confirm this hypothesis; thus, in the case of the complex bearing the symmetric ancillary ligand NNNtos(Py) (C_s point group) two singlets (six protons each) ascribable to the protons of the methyl carboxylate groups lying on the same side or on the opposite sides with respect to the substituent tosyl group of the uncoordinated amine nitrogen are detected. Conversely, the nonsymmetric NNNtos(Qui) ligand gives rise to only one isomer, in which four signals ascribable to the four different carboxymethyl protons are detected (C_1 point group). At room temperature a conformational rearrangement of the latter involving a fast flipping over and below the main molecular plane of the eight-membered cycle takes place, the symmetry of the molecule increases (C_1 to C_s point group), and the four singlets collapse into two singlets (COOCH_3 trans and cis to pyridine nitrogen). In principle, the complex derived from the symmetric NNNtos(Py) ligand would also collapse, owing to the increase of its symmetry (C_s to C_{2v} point group) upon increasing the temperature. However, the collapse was hardly observed at room temperature, since apparently NNNtos(Py) leads to the formation of a structure more firmly bound than that derived from NNNtos(Qui), as might also be deduced from the bond lengths reported in the X-ray crystal structure section.

The palladium(0) NNNtos(Qui) and NNNtos(Py) naphthoquinone complexes belong to the same point groups as the tmetc analogues. The molecular "freezing" of these species would, however, induce the formation of a differently populated pair of isomers (namely endo and exo), as represented in Chart 2. Again, the NNNtos(Qui) derivative displays an enhanced fluxionality with respect to the NNNtos(Py) complex, which "freezes" at 223 K. The ^{1}H NMR spectrum at 223 K of the latter displays the presence of the two isomers (ratio 4:1), as can be deduced from the presence of the two singlets ascribable to $C_6H_4-CH_3$ protons at 2.52 (major) and at 2.64 ppm (minor), and two olefin proton singlets at 4.64 (major) and 4.65 ppm (minor). Eventually the CH_2 endocyclic protons give rise to one AB (H_A, H_B: 4.94, 4.86 ppm, J = 14.9 Hz; major) and one AX system (H_A, H_X: 4.64, 4.03 ppm J = 14.8 Hz; minor). At variance, the NNNtos(Qui) naphthoquinone substrate hardly collapses, since its fluxionality is still operative even at 183 K. Thus, only one singlet (2.48 ppm) related to $C_6H_4-CH_3$ protons, one AB system (H_A, H_B: 4.92, 4.78 ppm, J = 6.4 Hz) for the olefin protons, and only one AX doublet of doublets (H_A, H_X: 5.55, 4.28 ppm, J = 4.28 Hz) due to CH_2 endocyclic protons are observable at all the achievable temperatures. It is noteworthy that, irrespective of the symmetric nature of the ancillary ligand, the CH_2 endocyclic protons give rise to AB or AX signals, owing to their diastereotopicity induced by the stereogenic "frozen" amine nitrogen.

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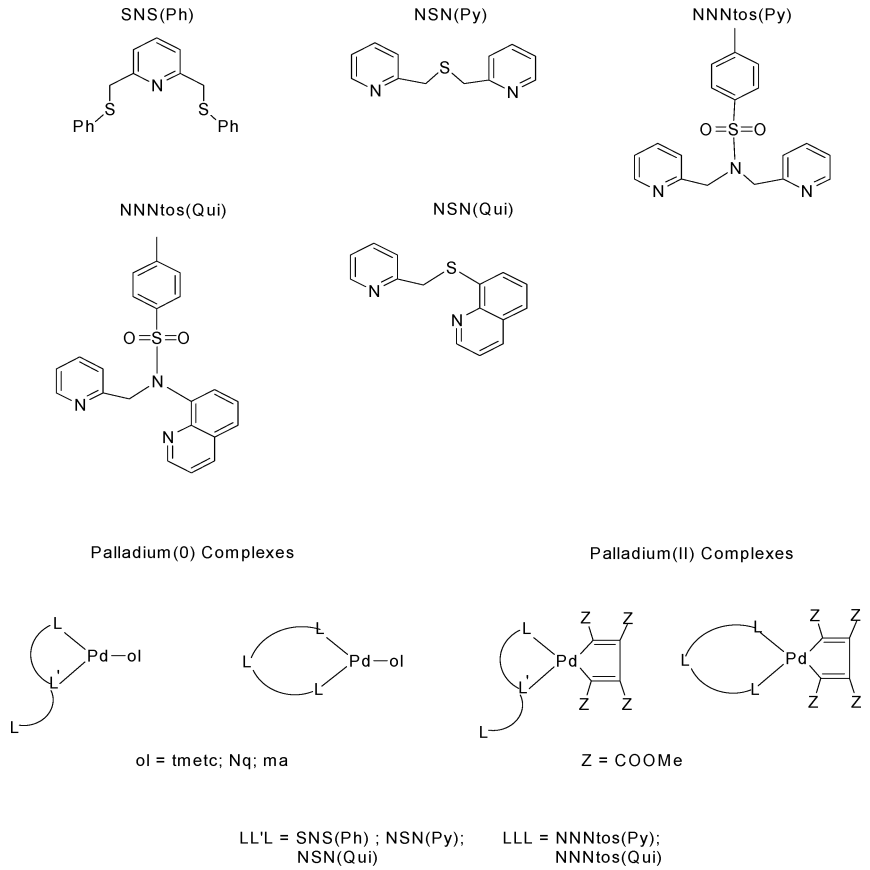
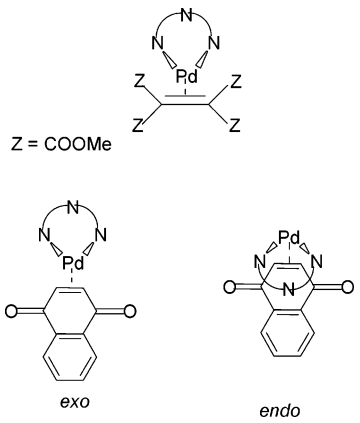
Chart 1



The complex [Pd(η^2-tmetc)(NSN(Qui))] undergoes a rearrangement in solution which is similar to that of palladium complexes bearing potentially terdentate NSN(Py) ligands, although the ligand NSN(Qui) is an unsymmetric molecule. The room-temperature ^{1}H NMR spectrum of the complex in CD_2Cl_2 displays only two singlets ascribable to olefin C═C(COOCH_3)$_2$ and endocyclic CH_2−S protons at 4.58 and 3.73 ppm, respectively. Apparently, the observed fluxionality is produced by a windshield-wiper movement involving an exchange between the nitrogen-carrying termini of the ligand (sulfur acts as a pivot) in a roundabout alternating movement (rearrangement via Y-shaped intermediate). The Y-shaped intermediate coupled with the inversion of the sulfur absolute configuration explains the molecular symmetry, which is destroyed when the decrease of temperature probably freezes the windshield-wiper movement with the consequent formation of a complex with an open wing. Since the doublet of doublets ascribable to the quinoline H^2 (assigned by means of H−H NOESY) shifts upfield (from 9.21 to 8.85 ppm; free ligand quinoline H^2 resonates at 8.95 ppm at 298 K) upon cooling of the solution, we advance the hypothesis that at 198 K the complex in solution could be represented as a species containing a bidentate ligand with only the pyridine nitrogen and the thioether sulfur coordinating to palladium. The sulfur absolute inversion is still operative, and only at 183 K does a partial coalescence of the CH_2−S signal indicate that this phenomenon is slowing down.

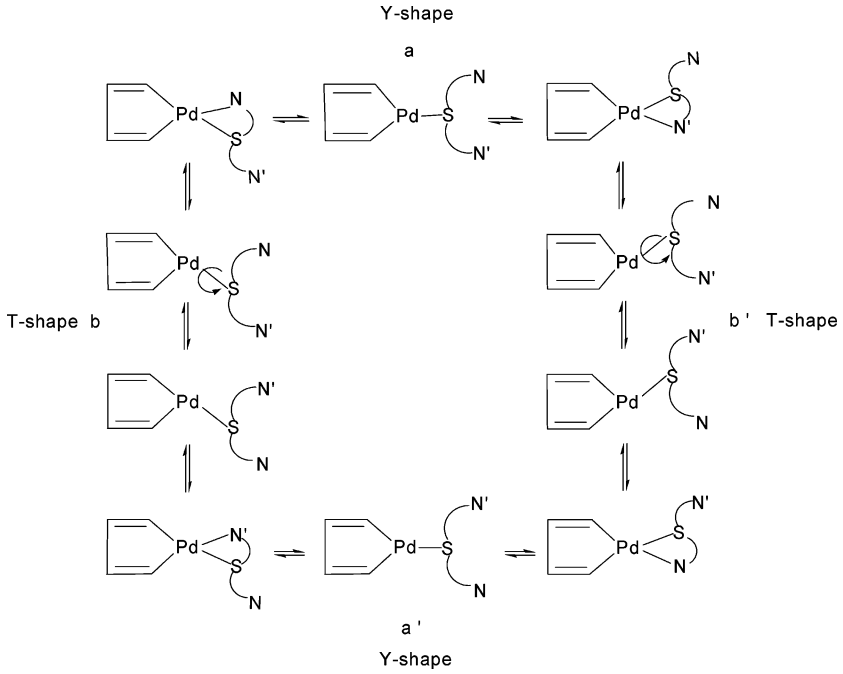
Chart 2



Solution Behavior of Pd(II) Cyclopentadienyl Complexes. The ^{1}H NMR spectra of the complexes [Pd(NNNtos(Py))(C$_4$(COOMe)$_4$)] and [Pd(NNNtos(Qui))(C$_4$(COOMe)$_4$)] indicate that no fluxional rearrangements are operative at room temperature. Thus, four singlets (three protons each) ascribable to the COOCH_3 protons are detected at 3.78, 3.63, 3.35, and 2.89 ppm in the case of the complex [Pd(NNNtos(Qui))(C$_4$(COOMe)$_4$)], indicating that the groups cis and trans to the quinoline fragment are not interchanging. The ^{1}H NMR spectrum of the complex [Pd(NNNtos(Py))(C$_4$(COOMe)$_4$)] at room temperature displays only two singlets at 3.62 and 3.07 ppm attributable to COOCH_3 protons, owing to the symmetry of the NNNtos(Py) ligand. This observation leads to the conclusion that also in the case of the palladium(II) derivatives the potentially terdentate nitrogen ligands act as bidentate, in which only the pyridine or quinoline nitrogen coordinates to the metal. The coordinating capability of amines to palladium(II) is well recognized but is also well-known to depend strongly on the basicity of the nitrogen.[3] Not surprisingly, the aliphatic nitrogen bearing the strongly electron-withdrawing tosyl group cannot compete efficiently with the aromatic nitrogen.

The complex [Pd(NSN(Qui))(C$_4$(COOMe)$_4$)] behaves differently from the previously described species. In this case a diffuse fluxionality is operative even at low temperature (178 K) and

Scheme 2



the course of the S−CH_2 system signal is quite complicated. As a matter of fact, the signal, which is a singlet at room temperature and an AB system between 235 and 210 K, reverts again into a broad singlet between 193 and 178 K. At the same time the aromatic part of the spectra hardly changes its symmetry. The interpretation we surmise takes into account sulfur inversion and ancillary ligand rotation, which represent the two main fluxional rearrangements in the case of complexes of palladium bearing potentially terdentate ligands. The appearance and the disappearance of the AB system are traced back to the formation at very low temperature of an asymmetric species bearing an uncoordinated nitrogen wing in which the central coordinated sulfur atom is not inverting its absolute configuration. Under these circumstances, irrespective of the coordinating nitrogen (quinoline or pyridine), two AB systems derived from the diasterotopic S−CH_2 would be detected. However, the sulfur absolute configuration inversion and the ancillary ligand rotational rearrangement usually represent very low energy processes if a dangling nucleophile is present in the palladium proximity and, for this reason, we are not able to "freeze" the process.[4] At the lowest reachable temperature we still observe the result of such dynamic processes and a broad singlet is detected. The broad singlet collapses first into an AB signal at intermediate temperature intervals and eventually into the final sharp singlet at room temperature when the rearrangement processes increase their rate.

The COOCH_3 proton signals are always detectable as two singlets, irrespective of the temperature and the signal shape of the potentially diasterotopic S−CH_2 system. At variance with the NNNtos(Py) and NNNtos(Qui) derivatives, in this case the central sulfur atom acting as a pivot allows different movements of the two wings carrying the nitrogen atom. In this respect the two surviving (at any temperature) COOCH_3 signals are easily recognized as those near to and far from the metal center.

Owing to the asymmetry of the two wings, it should be noted that at least two rearrangements of the ancillary ligand are operative at the same time (see Scheme 2). In one, a windshield-wiper movement through a Y-shaped intermediate mixes the carbon trans and the carbon cis to sulfur (routes a and a′). In the other, a rotation around the palladium−sulfur bond (T-shaped rearrangement) induces an alternate coordination of the two N wings, which would, however, maintain the reciprocal position between the sulfur and the carbon of the palladacyclopentadiene trans to each other (routes b and b′).

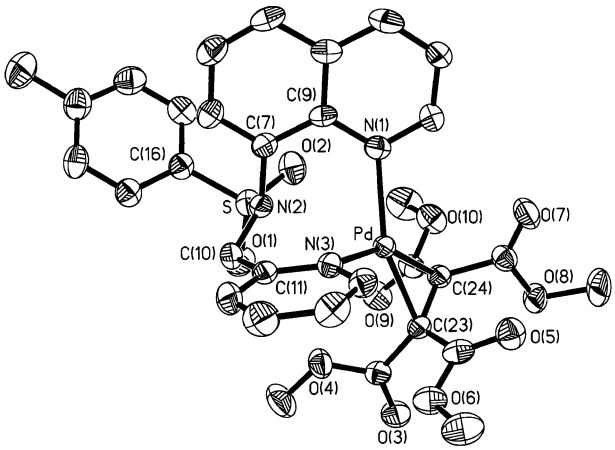


Figure 1. Structure of complex **1**. Thermal ellipsoids are shown at the 40% probability level; the crystallization solvent molecule and the hydrogen atoms are not shown.

X-ray Crystal Structures. Figures 1−4 give respectively the ORTEP[10] representations of the neutral complexes **1** ([Pd(NNNtos(Qui))(η^2-tmetc)]), **2** ([Pd(NNNtos(Py))(η^2-tmetc)]), **3** ([Pd(NNNtos(Qui))(η^2-Nq)]), and **4** ([Pd(NSN(Qui))(η^2-tmetc)]) (see Chart 1), together with the numbering scheme used, and Table 1 gives selected bond distances and angles. The Pd atoms lie at the center of an almost regular square-planar environment, whose vertices are occupied in **1**−**3** by N(1) and N(3) and by two carbon atoms (C(23)/C(24), C(20)/C(21), and C(23)/C(32) in **1**−**3**, respectively); in **4**, the donor set is made up by N(1), S, C(16), and C(17). These atoms do not deviate appreciably from the coordination (basal) plane, the largest departure being shown in **3** by C(23) (−0.09 Å) and C(32) (+0.09 Å). The Pd

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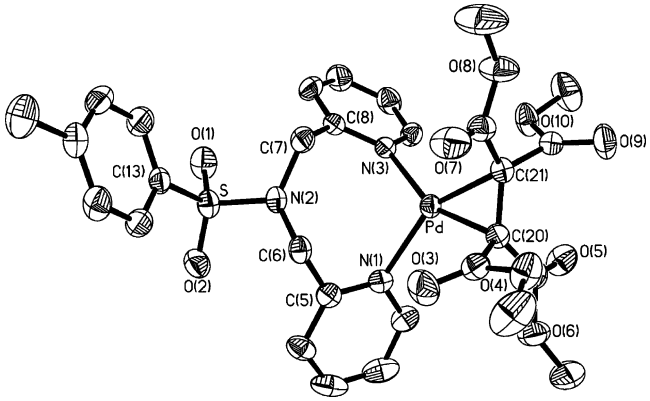

Figure 2. Structure of complex **2**. Thermal ellipsoids are shown at the 40% probability level; hydrogen atoms are not shown.

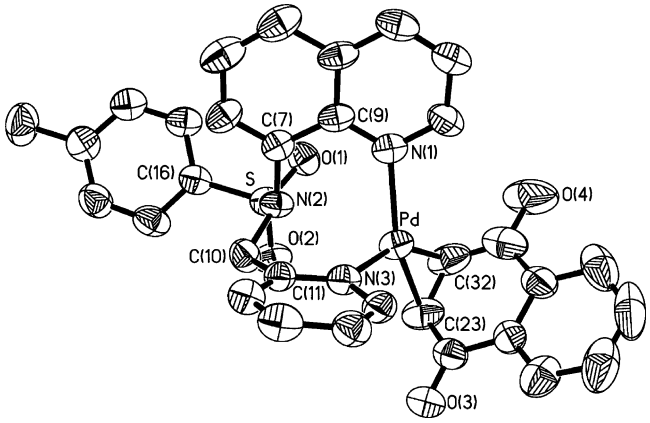

Figure 3. Structure of complex **3**. Thermal ellipsoids are shown at the 40% probability level; hydrogen atoms are not shown.

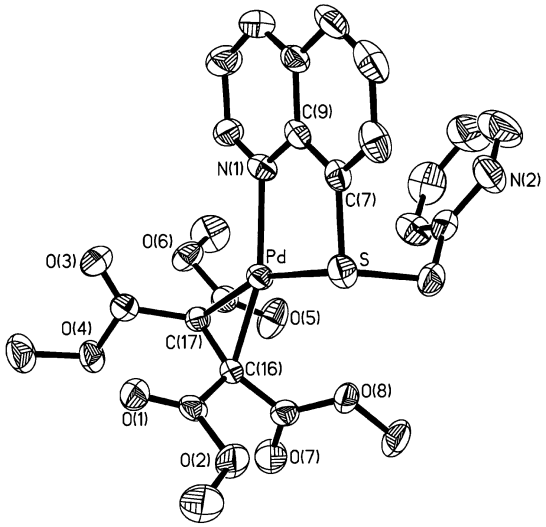

Figure 4. Structure of complex **4**. Thermal ellipsoids are shown at the 40% probability level; the crystallization solvent molecule and the hydrogen atoms are not shown.

atoms also do not deviate too much from the coordination plane (the largest deviation is 0.12 Å in **1**), and the sum of the valence angles around the metal is always close to 360° (the largest departure is 359.1° in **1** and **3**). Hence, there is no significant tetrahedral distortion.

In all complexes, a potentially terdentate ligand acts as a bidentate ligand, because the N(2) atoms lie too far from the metal center (2.846, 3.489, 2.785, and 4.840 Å in **1**−**4**, respectively). In **1** and **3** (in parentheses), the mean planes of the quinolyl, pyridyl, and tosyl moieties make dihedral angles of 52.8 (55.1), 80.0 (78.2), and 42.0° (57.9°), respectively, with the coordination plane; the quinolyl group makes dihedral angles of 87.3 (84.2) and 40.8° (31.0°) with the pyridyl and the tosyl moieties, respectively, and the pyridyl and the tosyl residues make an angle of 54.3° (65.7°) with each other.

In **2**, a pyridyl moiety replaces the quinolyl group. Here, the N(1)-pyridyl and N(3)-pyridyl (where N(1)- and N(3)-pyridyl are the pyridyl rings including N(1) and N(3)) and tosyl moieties make dihedral angles of 77.9, 77.8, and 79.5° with the basal plane. The N(1)-pyridyl and N(3)-pyridyl rings make an angle

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1−4

	Complex **1**		
Pd−N(1)	2.168(5)	S−O(1)	1.426(5)
Pd−N(3)	2.174(5)	S−O(2)	1.421(5)
Pd−C(23)	2.058(6)	S−N(2)	1.671(5)
Pd−C(24)	2.045(6)	S−C(16)	1.772(8)
C(23)−C(24)	1.444(8)		
N(1)−Pd−N(3)	92.2(2)	Pd−C(23)−C(25)	120.4(5)
C(23)−Pd−C(24)	41.2(2)	Pd−C(23)−C(27)	103.3(4)
N(1)−Pd−C(23)	157.2(2)	Pd−C(24)−C(29)	117.4(4)
N(3)−Pd−C(24)	149.8(2)	Pd−C(24)−C(31)	111.4(4)
Pd−N(1)−C(9)	124.2(4)	O(1)−S-O(2)	122.0(3)
Pd−N(3)−C(11)	123.8(4)	N(2)−S-O(1)	105.8(3)
C(10)−N(2)-C(7)	118.0(5)	N(2)−S-O(2)	106.6(3)
C(10)−N(2)-S	116.9(4)	N(2)−S-C(16)	105.0(3)
C(7)−N(2)-S	113.2(4)		
	Complex **2**		
Pd−N(1)	2.144(4)	S−O(1)	1.434(4)
Pd−N(3)	2.164(4)	S−O(2)	1.432(4)
Pd−C(20)	2.048(5)	S−N(2)	1.635(4)
Pd−C(21)	2.067(5)	S−C(13)	1.764(6)
C(20)−C(21)	1.454(7)		
N(1)−Pd−N(3)	96.3(1)	Pd−C(20)−C(22)	114.8(4)
C(20)−Pd−C(21)	41.4(2)	Pd−C(20)−C(24)	106.6(3)
N(1)−Pd−C(21)	147.5(2)	Pd−C(21)−C(26)	111.2(4)
N(3)−Pd−C(20)	157.3(2)	Pd−C(21)−C(28)	116.4(3)
Pd−N(1)−C(5)	121.3(3)	O(1)−S-O(2)	120.1(3)
Pd−N(3)−C(8)	124.4(3)	N(2)−S-O(1)	106.4(2)
C(6)−N(2)-C(7)	120.3(4)	N(2)−S-O(2)	106.7(2)
C(6)−N(2)-S	117.2(3)	N(2)−S-C(13)	107.5(2)
C(7)−N(2)-S	117.2(4)		
	Complex **3**		
Pd−N(1)	2.181(6)	S−O(1)	1.407(6)
Pd−N(3)	2.190(6)	S−O(2)	1.413(6)
Pd−C(23)	2.102(8)	N(2)−S	1.660(6)
Pd−C(32)	2.089(9)	S−C(16)	1.760(9)
C(23)−C(32)	1.43(1)		
N(1)−Pd−N(3)	93.1(2)	S−N(2)−C(10)	116.0(5)
C(23)−Pd−C(32)	39.9(4)	Pd−C(23)−C(24)	97.4(6)
N(1)−Pd−C(23)	155.0(3)	Pd−C(32)−C(31)	99.3(7)
N(3)−Pd−C(32)	150.8(3)	O(1)−S-O(2)	119.6(4)
Pd−N(1)−C(9)	125.8(5)	N(2)−S-O(1)	107.2(3)
Pd−N(3)−C(11)	124.9(5)	N(2)−S-O(2)	106.4(3)
C(7)−N(2)-C(10)	116.1(6)	N(2)−S-C(16)	106.7(4)
S−N(2)−C(7)	116.4(4)		
	Complex **4**		
Pd−S	2.360(2)	C(16)−C(17)	1.450(7)
Pd−N(1)	2.132(4)	S−C(7)	1.784(6)
Pd−C(16)	2.056(5)	S−C(10)	1.832(5)
Pd−C(17)	2.064(5)		
S−Pd−N(1)	83.7(1)	Pd−N(1)−C(9)	117.7(4)
C(16)−Pd−C(17)	41.2(2)	Pd−N(1)−C(1)	122.2(4)
N(1)−Pd−C(16)	159.5(2)	Pd−C(16)−C(18)	106.8(4)
S−Pd−C(17)	157.8(2)	Pd−C(16)−C(24)	118.3(4)
Pd−S−C(7)	97.7(2)	Pd−C(17)−C(20)	115.8(4)
Pd−S−C(10)	108.2(2)	Pd−C(17)−C(22)	107.3(4)

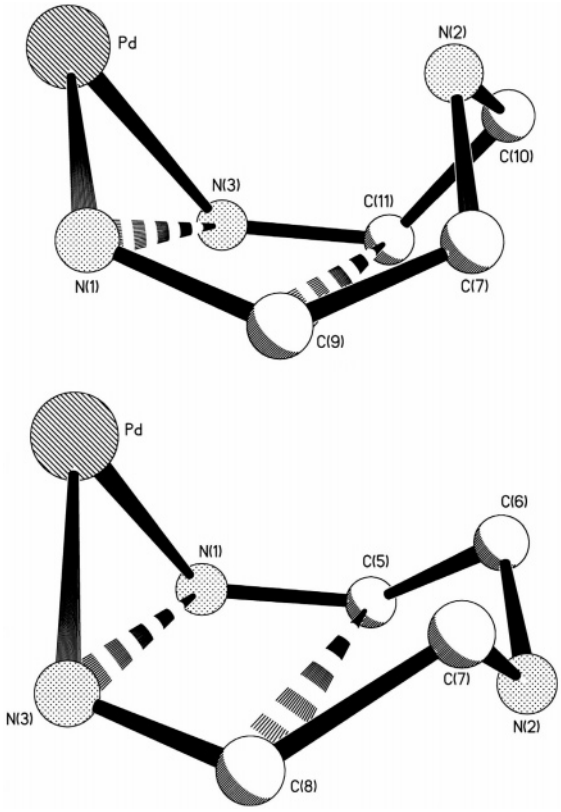

Figure 5. Puckering shown by the eight-membered cycle formed upon coordination by the NNNtos(Qui) ligand in **1** and **3** (top) and **2** (bottom).

of 71.4° with each other, while the same rings make angles of 46.2 and 39.6°, respectively, with the tosyl unit. In **4**, the tosyl group is missing. The mean planes of the quinolyl and pyridyl residues make dihedral angles of 9.9 and 39.1° with the coordination plane, while the quinolyl and the pyridyl rings make an angle of 41.8° with each other.

In **1**−**3**, the chelate ligands form an eight-membered ring upon coordination (Figure 5). However, the NNNtos(Qui) ligand in **1** and **3** (with the N(1), C(7), and C(9) atoms in a plane) gives rise to an arrangement more strained than that determined by the more flexible NNNtos(Py) in **2**. In the latter, the eight-membered cycle assumes an almost regular and rather relaxed boat−chair conformation, in which the N(1), N(3), C(5), C(8) atoms are coplanar, while Pd, C(6), N(2) and C(7) are out of the plane by +1.26, +0.87, +0.24 and +0.83 Å, respectively.

In **1** and **3**, two sets of four atoms, Pd, N(3), C(10), C(11) and N(1), N(2), C(7), C(9), define two planes making a dihedral angle of 77.2° in **1** and 83.4° in **3**, giving rise to a twist−boat−boat arrangement. A search in the Cambridge Crystallographic Database[11] for Pd complexes showing a similar eight-membered ring returned 12 structures. In these molecules, the boat−chair conformation largely predominates[12] over the twist−boat−boat one.[13] The twist−boat−boat arrangement in **1** and **3** should be due to the presence of an additional C−C partial double bond (missing in **2**), which reduces the conformational freedom of the cycle, increases the ring strain, and could explain, at least partially, the increased reactivity of **1** (see elsewhere in the paper).

At the opposite end, the NSN(Qui) ligand in **4** forms upon coordination a five-membered ring assuming an envelope (C_s) conformation, with the S, N(1), C(7), and C(9) atoms almost in the same plane (largest deviation 0.07 Å) and the Pd atom "at the flap", deviating by +0.24 Å.

In **3**, the tmetc ligand is replaced by a naphthoquinone (Nq) molecule. The mean plane of the quinone is almost perpendicular to the basal plane, making an angle of 85.9° with the latter. In the crystal, the Nq and the NNNtos(Qui) ligands adopt a mutually *exo* conformation. It is worth noting that only a few other Pd (or Pt) complexes having the Nq ligand have been deposited with the Cambridge Crystallographic Database.[14] In these compounds, the metal is always zerovalent and the ligand interacts with the metal in the η^2 mode, with the exception of the complex described by Selvakumar et al.[14] in 2002. The bond distances and angles involving Pd and the olefin C═C bond in Nq in **3** (Pd−C = 2.102, 2.089 Å, C═C = 1.43 Å, and C−Pd−C = 39.9°) compare well with those described by Mestroni et al.[14] in 2001 (2.070, 2.088, and 1.42 Å and 40.0°).

With respect to the bond distances around Pd, the values found in **1**−**4** also fit within the reported ranges for Pd(0) neutral complexes. In particular, Pd−C distances fall in the lower half of the known range (2.029−2.167 Å), except for **3** (see above); the opposite is true for Pd−N bond lengths (range 2.086−2.202 Å), except for **4**, where the single Pd−N bond is 2.132(4) Å. A more detailed inspection of existing data indicates that our values are similar to those reported in 2003 by Stahl and co-workers[15] in a series of nitrostyrene derivatives (Pd−C between 2.039 and 2.086 Å, Pd−N between 2.145 and 2.182 Å).

In **1**−**3**, one of the Pd−C/Pd−N distances is slightly longer than the other and the arrangement around Pd is such that a shorter Pd−C distance is trans to a longer Pd−N bond and vice versa, the longer Pd−N distance always involving N(3). The Pd−C and Pd−N bond lengths in **3** are, on the average, longer by ca. 0.04 and 0.02 Å, respectively, than those found in **1** and **2**. This might be due to steric repulsions between the NNNtos-

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Table 2. Second-Order Rate Constants (mol^{-1} dm^3 s^{-1}) for the Reaction of the Complexes [Pd(η^2-ol)(LL′L)] with DMA in $CHCl_3$ at 25 °C

complex	k_2
[Pd(η^2-tmetc)(SNS(Ph))]	0.272 ± 0.005
[Pd(η^2-tmetc)(NSN(Py))]	0.079 ± 0.001
[Pd(η^2-Nq)(NSN(Py))]	8.3 ± 3.1[a]
[Pd(η^2-tmetc)(NSN(Qui))]	0.071 ± 0.001
[Pd(η^2-tmetc)(NNNtos(Py))]	0.087 ± 0.002
[Pd(η^2-tmetc)(NNNtos(Qui))]	7.1 ± 0.2
[Pd(η^2-Nq)(NNNtos(Py))]	fast
[Pd(η^2-Nq)(NNNtos(Qui))]	fast

[a] See the Supporting Information.

(Qui) and Nq ligands in **3**, leading to a less tight binding to the metal center.

As for nonbonding interactions, a careful investigation revealed no feature worthy of comment in any of the complexes described here.

Kinetic and Mechanistic Study. The mechanistic studies involving the oxidative coupling of DMA with complexes of the type [Pd(η^2-ol)(LL′L)] (ol = tmetc, LL′L = SNS(Me), SNS(Ph), NSN(Py), NSN(Qui), NNNtos(Py), NNNtos(Qui); ol = Nq, LL′L = NSN(Py), NNNtos(py), NNNtos(Qui)) were carried out by UV/vis techniques under pseudo-first-order conditions. In every case preliminary NMR studies were performed in order to unequivocally establish the reaction progress and the nature of the reagents and products. In a typical experiment a microaliquot of a DMA solution ($CHCl_3$) was added to 3 mL of a prethermostated solution ($CHCl_3$) of the complex under study ($[Pd]_0 \approx 10^{-4}$ mol dm^{-3}, $[DMA]_0 = 20[Pd]_0$). The reaction progress was followed by recording the spectra between 220 and 400 nm at different times or the absorbance at a suitable fixed wavelength in order to ensure the largest spectral change. In the cases in which the tmetc derivatives are involved, the absorbance change associated with the reactions studied under pseudo-first-order conditions is described by the monoexponential rate law

$$A_t = A_\infty + (A_0 - A_\infty)e^{-k_{obs}*t}$$

where A_t, A_∞, and A_0 represent the absorbance of the reaction mixture at time t, at the end, and at the beginning of the reaction and k_{obs} is the observed pseudo-first-order rate constant. Table 2 summarizes the second-order rate constants determined by linear regression of the corresponding k_{obs} value vs the DMA concentration. In Table 2 are also reported the results of the reactions involving the Nq derivatives which are too fast to be followed by conventional methods. The case of the reaction of the complex [Pd(η^2-Nq)(NSN(Py))] and DMA will be dealt with further on.

As can be seen in Table 2, the reaction behavior of the olefin complexes bearing potentially terdentate ligands is similar to that of the palladium(0) bidentate pyridylthioether substrates. In this respect the mechanism parallels that proposed so far, which takes into account the slow associative formation of a monoalkyne intermediate that rapidly reacts with a further alkyne molecule to give the palladacyclopentadienyl species:[4]

$$[\underset{\mathbf{A}}{Pd(\eta^2\text{-ol})(LL'L)}] \underset{k_r[ol]}{\overset{k_2[DMA]}{\rightleftharpoons}} [\underset{\mathbf{B}}{Pd(\eta^2\text{-DMA})(LL'L)}] \xrightarrow{k_3[DMA]} [\underset{\mathbf{P}}{Pd(LL'L)(C_4(COOMe)_4)}]$$

Under the steady-state approximation ($d[\mathbf{B}]/dt = 0$; $k_3[DMA] \gg k_r[ol]$) the rate law becomes

$$k_{obs} = k_2[DMA]_0$$

Moreover, the measured rate constants for these complexes are not very different from those determined in the case of the bidentate pyridylthioether substrates, the values in Table 2 being comparable with the values in ref 4. Thus, entry 1 of Table 2 is traced back to the reaction rate of the complexes [Pd(η^2-tmetc)(HN−SMe)] (0.2 mol^{-1} dm^3 s^{-1}) and [Pd(η^2-tmetc)(HN−SPh)] (0.137 mol^{-1} dm^3 s^{-1}), while entries 2, 4, and 5 react similarly to the species [Pd(η^2-tmetc)(MeN−SMe)] and [Pd(η^2-tmetc)(MeN−SPh)] (0.09 and 0.114 mol^{-1} dm^3 s^{-1}, respectively). Quite surprisingly, the reactivity of the complex [Pd(η^2-tmetc)(NNNtos(Qui))] is much higher than those of all of the other tmetc complexes. From considerations on the basicity of the pyridine vs quinoline nitrogen (pK_a(Py) = 5.23, pK_a(Qui) = 4.90), no clear-cut conclusions can be reached. We have also tried to determine the pK_a values of pyridine and quinoline bound together into a polydentate ligand, resolving the microconstant system for related ligands (see Supporting Information), but again no clues have been obtained, since although the pK_a values change, their mutual ratio remains almost the same. In our opinion the enhanced reactivity of the complex derives from the rigidity of the ligand arm bearing the quinoline moiety, which under the alkyne attack easily undergoes decoordination, any conformational rearrangement being prevented. The crystal structure determination appears to confirm this hypothesis. As a matter of fact, similar reactivity can be observed when complexes of the type [Pd(η^2-tmetc)(ClN−SR)] react with DMA. The decreased basicity of the pyridine nitrogen under the influence of the chlorine atom in position 6 of the pyridine ring entails ring opening and a consequent increase in reactivity.[4] Conversely, the ligands bearing two pyridine groups (in the case of the related eight-membered cycle) or the thioetheric sulfur display a marked flexibility. Thus, the consequent reduced tendency to ring opening increases the steric requirement of the associative reaction. Moreover, we tried to determine the reactivity of the complexes [Pd(η^2-Nq)(NNNtos(Py))] and [Pd(η^2-Nq)(NNNtos(Qui))], but the reduced steric demand of the naphthoquinone induces an increase in rate and, consequently, the reactions cannot be followed by conventional methods.

The complex [Pd(η^2-Nq)(NSN(Py))] reacts with DMA, and in this case two consecutive reactions can be detected by UV/vis techniques. The increase of the first reaction rate due to the decreasing olefin steric hindrance allows detection of the faster second step. This fact provides a close insight into the intimate mechanism governing these reactions. As a matter of fact, the rates of the two reactions (Λ_1, Λ_2) are both dependent on the DMA and naphthoquinone concentrations, as would be expected of the mechanism in Scheme 1.

Solution of the system (see the Supporting Information) leads to determination of the rate constants, which are $k_r = 12.3 \pm 2.5$, $k_2 = 8.3 \pm 3.1$, and $k_3 = 11.1 \pm 4.9$ mol^{-1} dm^3 s^{-1} (or $k_2 = 11.1$ and $k_3 = 8.3$ mol^{-1} dm^3 s^{-1}).[16] The k_3 value, which is related to the addition of a second alkyne molecule to the intermediate monoalkyne species, justifies the steady-state approximation in the cases of the slow reactions of Table 2. From the k_2 and k_r values one may obtain the equilibrium constant related to the exchange between the olefin Nq and the alkyne DMA ($K_{exc} = 0.68 \pm 0.29$ ($k_2 = 8.3$); $K_{exc} = 0.90 \pm 0.44$

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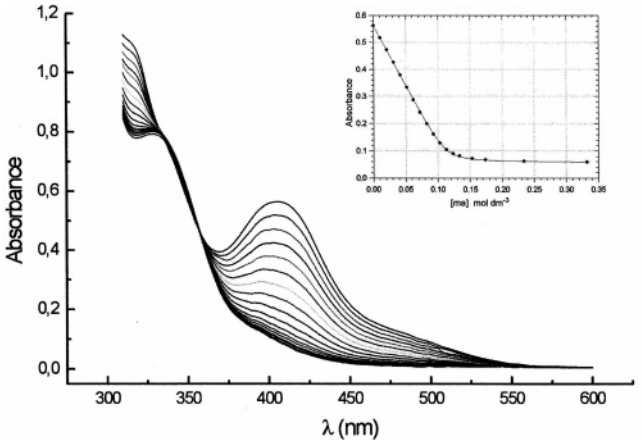

Figure 6. UV−vis absorbance changes for the spectrophotometric titration of [Pd(η^2-Nq)(MeN−S*t*Bu)] with maleic anhydride (ma) in $CHCl_3$ at 25 °C. In the top inset the best fitting for the reaction under study at λ 419 nm is reported.

($k_2 = 11.1$)). It is apparent that knowledge of the relative coordination strength between Nq and DMA would represent a check on the internal consistency of the kinetic determinations. Since we already determined the equilibrium constant for the olefin exchange between ma (maleic anhydride) and DMA according to eq 1 ($K_{1exc} = 0.014 \pm 0.003$),[4]

$$[Pd(\eta^2\text{-ma})(MeN-StBu)] + DMA \leftrightarrow [Pd(\eta^2\text{-DMA})(MeN-StBu)] + ma \quad (1)$$

the determination of the equilibrium constant of eq 2 would provide the equilibrium constant of eq 3 since $K_3(exc) = [K_1(exc)][K_2(exc)]$.

$$[Pd(\eta^2\text{-Nq})(MeN-StBu)] + ma \leftrightarrow [Pd(\eta^2\text{-ma})(MeN-StBu)] + Nq \quad (2)$$

$$[Pd(\eta^2\text{-Nq})(MeN-StBu)] + DMA \leftrightarrow [Pd(\eta^2\text{-DMA})(MeN-StBu)] + Nq \quad (3)$$

The value determined for $K_2(exc)$ is 88 ± 7.4 (see Supporting Information). Thus, the ensuing $K_3(exc)$ value is 1.23 ± 0.28, which is in good agreement with the average value of 0.8 ± 0.5 (0.68−0.90) calculated from the kinetic data. As a matter of fact, it is well-known that the nature of the ancillary ligand scarcely influences the olefin exchange constants,[6] so that the calculated value represents a very good estimate of the K_{exc} value relating to the exchange of the same unsaturated species in substrates with different ancillary ligands. At the same time, however, this value does not allow any choice between the k_2 values (8.3−11.1) determined so far due to the proximity of the their values.

Conclusions

From the present study the following may be deduced.

(a) The ancillary ligands of the types SNS and NSN give palladium(0) olefin complexes in which the cycle formed by metal and the ancillary ligand is a *five*-membered ring with an uncoordinated dangling arm, which induces a massive fluxionality.

(b) The ancillary ligands of the type NNN form *eight*-membered palladium(0) olefin complexes, which appear to be particularly strained in the case of the complex [Pd(η^2-tmetc)(NNNtos(Qui))]. In no case is coordination of the central nitrogen atom observed.

(c) The overall reactivity of the palladium(0) olefin complexes toward alkyne attack to give palladacyclopentadiene complexes was confirmed to be strongly dependent on the steric and electronic characteristics of the leaving olefin and of the ancillary ligand (entries 3, 7, and 8 in Table 2)[4] but independent of the size of the cycle constituted by the metal and the ancillary ligand (entries 5 and 6 in Table 2).

(d) The presence of a bidentate or of a potentially terdentate ligand does not induce a mechanistic change in the alkyne attack, at variance with the previously studied reactions of olefin exchange.[6]

(e) The reactivity of the complex is influenced (ceteris paribus) by the attitude of the ancillary ligand to cycle opening with concomitant attack of the entering alkyne on the vacant coordination site (ref 4 and entry 6 in Table 2).

Experimental Section

Preparation of Ligands. The syntheses of the ligands MeN−S*t*Bu,[17] SNS(Ph),[18] and NSN(Py)[6] were carried out according to published procedures. All other chemicals were commercial grade and were purified or dried by standard methods where required.

8-((2-Pyridylmethyl)thio)quinoline (NSN(Qui)). The synthesis reported below represents the revised version of a published procedure.[19]To 0.988 g (5 mmol) of 8-mercaptoquinoline hydrochloride and 0.861 g (5.25 mmol) of 2-picolyl chloride hydrochloride in 30 mL of distilled DMF was added 1.43 mL (10.25 mmol) of TEA. The ammonium salt was removed by filtration, and 0.829 g (6 mmol) of K_2CO_3 was added to the solution. The resulting mixture was stirred under an inert atmosphere (N_2) for 24 h at 50 °C and the solvent removed under reduced pressure. The residue was suspended in H_2O and extracted with CH_2Cl_2, and the extract was washed with an aqueous solution of Na_2CO_3 and H_2O. The organic phase was separated, dried over Na_2SO_4, filtered, and dried under vacuum. The purification of the crude product was achieved by flash chromatography through a silica column with a 1:1 CH_2Cl_2/Et_2O mixture as eluent. Concentration under vacuum of the eluate yields 1.135 g (4.5 mmol) of the title compound as a pale yellow powder. Yield 90%.

IR (KBr pellet): ν_{C-H} 3061.5, $\nu_{C=N}$ 1586.6, $\nu_{C=C}$ 1472.6, 1445.8 cm^{-1}. ^1H NMR ($CDCl_3$, $T = 298$ K, ppm): thiomethyl protons, δ 4.62 (s, 2H, pyr CH_2S); pyridine and quinoline protons δ 7.16 (ddd, 1H, $H^{5'}_{py}$, $J_{5'-4'} = 5.76$ Hz, $J_{5'-3'} = 2$ Hz), 7.44 (m, 2H, H^3_{qui}, $H^{3'}_{py}$), 7.59 (m, 4H, H^5_{qui}, H^6_{qui}, H^7_{qui}, $H^{4'}_{py}$), 8.14 (dd, 1H, H^4_{qui}, $J_{4-3} = 8.42$ Hz), 8.57 (d, 1H, $H^{6'}_{py}$, $J_{6'-5'} = 4.39$ Hz), 8.97 (dd, 1H, H^2_{qui}, $J_{2-3} = 4.40$ Hz, $J_{2-4} = 1.83$ Hz). ^{13}C NMR ($CDCl_3$, $T = 298$ K, ppm): thiomethyl carbon, δ 37.56 (pyr *C*H_2S); pyridine carbons, δ δ 121.98 ($C^{5'}_{py}$), 122.88 ($C^{3'}_{py}$), 136.69 ($C^{4'}_{py}$), 148.96 ($C^{6'}_{py}$), 157.60 ($C^{2'}_{py}$); quinoline carbons, δ δ 121.55 (C^3_{qui}), 124.25 (C^5_{qui}), 125.02, 126.56 (C^6_{qui}, C^7_{qui}), 128.15 (C^8_{qui}), 136.26 (C^4_{qui}), 137.55 (C^{8a}_{qui}), 145.50 (C^{4a}_{qui}), 149.18 (C^2_{qui}).

Sodium *N*-Tosyl-8-quinolinamide. To 0.23 g (10 mmol) of Na dissolved in 100 mL of EtOH was added 2.984 g (10 mmol) of *N*-tosyl-8-aminoquinoline. The resulting mixture was stirred at boiling temperature for 2 h and eventually cooled to 0 °C. The precipitate was filtered off, washed with cold Et_2O, and dried under vacuum. Yield 99% (3.203 g, 10 mmol, white powder).

8-*N*-Tosyl-*N*-(2-pyridylmethyl)quinoline (NNNtos(Qui)). To 1.80 g (11 mmol) of 2-picolyl chloride hydrochloride in 50 mL of freshly distilled DMF was added 1.53 mL (11 mmol) of TEA. After

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filtration of the ammonium salt, 3.20 g (10 mmol) of sodium *N*-tosyl-8-quinolinamide was added. The resulting mixture was stirred under an inert atmosphere (N_2) for 24 h at 80 °C. The solvent was removed under reduced pressure, and the residue was ground in H_2O and extracted with CH_2Cl_2 and the extract washed with an aqueous solution of Na_2CO_3 and H_2O. The organic phase was separated, dried over Na_2SO_4, filtered, and dried under vacuum. The purification of the crude product was achieved by flash chromatography through a silica column with a 1:1 CH_2Cl_2/Et_2O mixture as eluent. Concentration under vacuum of the eluate gives 2.416 g (6.2 mmol) of the title compound as a pale yellow powder. Yield: 60%.

IR (KBr pellet): ν_{C-H} 3072.0, 3012.8, 2979.9, 2920.7, $\nu_{C=N}$ 1591.2, $\nu_{C=C}$ 1505.7, 1472.8, 1445.4 cm^{-1}. ^1H NMR ($CDCl_3$, T = 298 K, ppm): methyl protons, δ 2.36 (s, 3H, $-CH_3$); aminomethyl protons, 5.36 (s, 2H, pyr CH_2N); pyridine protons, 7.06 (t, 1H, $H^{5'}_{py}$, $J_{5'-6'}$ = 4.43 Hz), 7.64 (t, 1H, $H^{4'}_{py}$, $J_{3'-4'}$ = 7.79 Hz), 7.83 (d, 1H, $H^{3'}_{py}$, $J_{4'-5'}$ = 7.79 Hz), 8.36 (d, 1H, $H^{6'}_{py}$); phenyl protons, 7.10, 7.56 (AB system, H^c, H^b, 4H), quinoline protons 7.26 (dd, 1H, H^3_{qui}, J_{3-2} = 4.15 Hz), 7.42 (t, 1H, H^6_{qui}, $J_{6-7} = J_{6-5}$ = 7.82 Hz), 7.73 (m, 2H, H^7_{qui}, H^5_{qui}), 8.05 (dd, 1H, H^4_{qui}, J_{3-4} = 8.29 Hz), 8.53 (dd, 1H, H^2_{qui}, J_{2-4} = 1.32 Hz). ^{13}C NMR ($CDCl_3$, T = 298 K, ppm): methyl carbon, δ 21.38 ($-CH_3$); aminomethyl carbon, 57.14 (pyr CH_2N); pyridine carbons, 121.98 ($C^{5'}_{py}$), 122.46 ($C^{3'}_{py}$), 136.48 ($C^{4'}_{py}$), 18.74 ($C^{6'}_{py}$), 157.97 ($C^{2'}_{py}$), quinoline carbons, 121.01 (C^3_{qui}), 125.89 (C^6_{qui}), 128.69 (C^7_{qui}), 129.35 (C^8_{qui}), 133.28 (C^5_{qui}), 135.97 (C^4_{qui}), 144.75 (C^{4a}_{qui}), 149.44 (C^2_{qui}), phenyl carbons, δ 127.95 (C^b_{ph}), 128.82 (C^c_{ph}), 135.92 (C^a_{ph}), 142.83 (C^d_{ph}).

Sodium *N*-2-Pyridylmethyltosylamide. This compound was synthesized in a way similar to that for sodium *N*-tosyl-8-quinolinamide using *N*-tosyl-2-(aminomethyl)pyridine and EtONa.[20]

***N*-Tosylbis(2-pyridylmethyl)amine (NNNtos(Py)).** This ligand was synthesized in a way similar to that for NNNtos(Qui) using sodium *N*-2-pyridylmethyl tosylamide. Yield: 56%.

IR (KBr pellet): ν_{C-H} 3060.0, 3010.2, 2912.4, 2857.1, $\nu_{C=N}$ 11593.2, $\nu_{C=C}$ 1503.0, 1470.0, 1432.6 cm^{-1}. ^1H NMR ($CDCl_3$, T = 298 K, ppm): methyl protons, δ 2.44 (s, 3H, $-CH_3$); aminomethyl protons, 4.58 (AB system, 4H, pyr CH_2N); pyridine protons, 7.08 (ddd, 1H, H^5_{py}, J_{5-6} = 4.9 Hz,, J_{5-4} = 7.66 Hz), 7.34 (dd, 1H, H^3_{py}, J_{3-4} = 7.66, J_{3-5} = 1.13 Hz), 7.54 (td, 1H, H^4_{py}), 8.38 (dd, 1H, H^6_{py}, J_{6-4} = 1.76 Hz); phenyl protons, 7.45, 7.83 (AB system, H^c, H^d, 4H). ^{13}C NMR ($CDCl_3$, T = 298 K, ppm): methyl carbon, 21.42 ($-CH_3$); aminomethyl carbon, 53.96 (pyr CH_2N); pyridine carbons, 122.16 (C^5_{py}), 122.57 (C^3_{py}), 136.29 (C^4_{py}), 148.89 (C^6_{py}), 156.34 (C^2_{py}), phenyl carbons, δ 127.32 (C^b_{ph}), 129.49 (C^c_{ph}), 136.42 (C^a_{ph}), 143.29 (C^d_{ph}).

Synthesis of Pd(0) Olefin Complexes Bearing Terdentate Ligands. The synthesis of the complexes [Pd(η^2-tmetc)(SNS(Ph))], [Pd(η^2-tmetc)(NSN(Py))], and [Pd(η^2-Nq)(NSN(Py))] was carried out according to published procedures.[6]

[Pd(η^2-tmetc)(NSN(Qui))]. A 0.107 g portion (0.424 mmol) of the ligand NSN(Qui), 0.111 g (0.427 mmol) of the olefin tmetc, and 0.2 g (0.193 mmol) of $Pd_2DBA_3{\cdot}CHCl_3$ were dissolved under an inert atmosphere (N_2) in 15 mL of anhydrous acetone. The resulting solution was stirred for 1 h, treated with activated charcoal, and filtered off on a Celite filter. Concentration under reduced pressure and addition of Et_2O gives 0.2311 g (0.373 mmol) of the title product as yellow microcrystals. Yield: 94%.

IR (KBr pellet): ν_{C-H} 3006.2, 2953.6, 2841.7, $\nu_{C=O}$ 1736.0 1696.5 cm^{-1}. ^1H NMR ($CDCl_3$, T = 298 K, ppm): methyl ester protons, δ 3.77 (s, 12H, $-COOCH_3$); thiomethyl protons, δ 4.62 (s, 2H, pyr CH_2S); pyridine protons, δ 6.85 (dd, 1H, $H^{5'}_{py}$, $J_{5'-6'}$ = 4.99 Hz), 7.43 (td, 1H, $H^{4'}_{py}$, $J_{4'-5'}$ = 7.44 Hz, $J_{4'-6'}$ = 1.88 Hz), 7.94 (m, 3H, $H^{6'}_{py}$, $H^{3'}_{py}$, H^7_{qy}); quinoline protons, δ 7.44 (dd, 1H, H^3_{qui}, J_{3-2} = 4.71 Hz), 7.56 (t, 1H, H^6_{qui}, J_{6-7} = 7.91 Hz), 8.23 (dd, 1H, H^4_{qui}, J_{4-3} = 8.20 Hz), 7.85 (d, 1H, H^5_{qui}, J_{5-6} = 7.91 Hz), 9.25 (dd, 1H, H^2_{qui}, J_{2-4} = 1.22 Hz). ^{13}C NMR ($CDCl_3$, T = 298 K, ppm): thiomethyl carbon, δ 46.88 (pyr CH_2S); methyl ester carbons, δ 52.30 ($-COOC^{\alpha}H_3$) ($-COOC^{\beta}H_3$); vinyl carbons, δ 59.77 (C=C), pyridine carbons, δ 122.01 ($C^{5'}_{py}$), 125.43 ($C^{3'}_{py}$), 136.44 ($C^{4'}_{py}$), 147.72 ($C^{6'}_{py}$), 155.98 ($C^{2'}_{py}$); quinoline carbons, δ 122.46 (C^3_{qui}), 127.41 (C^6_{qui}), 129.28 (C^{4a}_{qui}), 130.06 (C^5_{qui}), 131.31 (C^8_{qui}), 137.90 (C^4_{qui}), 138.24 (C^7_{qui}), 147.96 (C^{8a}_{qui}), 155.14 (C^2_{qui}); carbonyl carbons, δ 169.63 ($-COOCH_3$). Anal. Calcd for $C_{25}H_{24}N_2O_8PdS$: C, 48.51; H, 3.91; N, 4.53. Found: C, 48.65; H, 4.01; N, 4.44.

The following complexes were synthesized in an analogous way using the appropriate ligand and olefin.

[Pd(η^2-tmetc)(NNNtos(Qui))]. Yield: 91% (yellow microcrystals). IR (KBr pellet): ν_{C-H} 3072.0, 2947.0, 2861.4, $\nu_{C=O}$ 1716.3, $\nu_{C=N}$ 1604.4 cm^{-1}. ^1H NMR ($CDCl_3$, T = 298 K, ppm): methyl protons, δ 2.43 (s, 3H, $-CH_3$); methyl ester protons, δ 3.63, 3.84 (s, 12H, $-COOCH_3$); aminomethyl protons, δ 4.49, 6.31 (AB system, 2H, pyr CH_2N); pyridine protons, δ 6.90 (td, 1H, $H^{5'}_{py}$, $J_{5'-6'}$ = 5.28 Hz), 7.06 (d, 1H, $H^{3'}_{py}$, $J_{3'-4'}$ = 7.66 Hz), 7.42 (td, 1H, $H^{4'}_{py}$, $J_{4'-5'}$ = 6.45 Hz, $J_{4'-6'}$ = 1.7 Hz), 8.44 (dd, 1H, $H^{6'}_{py}$); phenyl protons, δ 7.25, 7.50 (AB system, H^c, H^b, 4H); quinoline protons, δ 7.51 (dd, 1H, H^3_{qui}, J_{3-2} = 4.71 Hz), 7.14 (t, 1H, H^6_{qui}, J_{6-7} = 7.45 Hz), 6.75 (dd, 1H, H^7_{qui}, J_{7-5} = 1.32 Hz), 8.06 (dd, 1H, H^4_{qui}, J_{4-3} = 8.34 Hz), 7.64 (dd, 1H, H^5_{qui}, J_{5-6} = 8.2 Hz),10.54 (dd, 1H, H^2_{qui}, J_{2-4} = 1.65 Hz). ^{13}C NMR ($CDCl_3$, T = 298 K, ppm): methyl carbon, δ 21.46 ($-CH_3$); methyl ester carbons, δ 51.45, 52.33 ($-COOCH_3$); aminomethyl carbon, δ 56.67 (pyr CH_2N); pyridine carbons, δ 122.60 ($C^{5'}_{py}$), 125.00 ($C^{3'}_{py}$), 136.85 ($C^{4'}_{py}$), 151.36 ($C^{6'}_{py}$), 155.35 ($C^{2'}_{py}$); quinoline carbons, δ 122.60 (C^3_{qui}), 125.00 (C^6_{qui}), 129.01 (C^7_{qui}), 129.55 (C^{8a}_{qui}), 129.68 (C^5_{qui}), 134.61 (C^8_{qui}), 136.65 (C^4_{qui}), 145.67 (C^{4a}_{qui}), 156.79 (C^2_{qy}); phenyl carbons, δ 128.76 (C^b_{ph}), 129.18 (C^c_{ph}), 133.20 (C^a_{ph}), 143.76 (C^d_{ph}); carbonyl carbons, δ 170.22 ($-COOCH_3$). Anal. Calcd for $C_{32}H_{31}N_3O_{10}PdS$: C, 50.83; H, 4.13; N, 5.56. Found: C, 50.68; H, 4.21; N, 5.46.

[Pd(η^2-tmetc)(NNNtos(Py))]. Yield: 89% (yellow microcrystals). IR (KBr pellet): ν_{C-H} 2993.1, 2953.6, 2920.7, $\nu_{C=O}$ 1729.4, 1689.9, $\nu_{C=N}$ 1604.4 cm^{-1}. ^1H NMR ($CDCl_3$, T = 298 K, ppm): methyl protons, δ 2.50 (s, 3H, $-CH_3$); methyl ester protons, δ 3.53, 3.68 (s, 12H, $-COOCH_3$); aminomethyl protons, δ 4.97, 5.36 (AB system, 2H, pyr CH_2N); pyridine protons, δ 7.21 (dd, 1H, H^5_{py}, J_{5-4} = 10 Hz), 7.66 (m, 2H, H^3_{py}, H^4_{py}), 8.89 (d, 1H, H^6_{py}, J_{6-5} = 5 Hz); phenyl protons, δ 7.38, 7.74 (AB system, H^c, H^d, 4H). ^{13}C NMR ($CDCl_3$, T = 298 K, ppm): methyl carbon, 21.16 ($-CH_3$); aminomethyl carbon, 59.39 (pyr CH_2N); methyl ester carbons, δ 51.64 ($-COOCH_3$); pyridine carbons, δ 123.53 (C^5_{py}), 126.37 (C^3_{py}), 137.34 (C^4_{py}), 150.99 (C^6_{py}), 158.41 (C^2_{py}); phenyl carbons, δ 126.92 (C^b_{ph}), 129.97 (C^c_{ph}), 136.01 (C^a_{ph}), 144.23 (C^d_{ph}). Anal. Calcd for $C_{29}H_{31}N_3O_{10}PdS$: C, 48.37; H, 4.34; N, 5.84. Found: C, 48.57; H, 4.41; N, 5.79.

[Pd(η^2-Nq)(NNNtos(Qui))]. Yield: 83% (red microcrystals). IR (KBr pellet): ν_{C-H} 3058.9, 2920.7, 2868.0, $\nu_{C=O}$ 1624.1, 1584.6 cm^{-1}. ^1H NMR ($CDCl_3$, T = 298 K, ppm): methyl protons, δ 2.48 (s, 3H, $-CH_3$); aminomethyl protons, δ 4.39, 5.62 (AB system, 2H, pyr CH_2N); naphthoquinone protons, δ 4.91, 5.19 (AB system, 2H), 7.55 (qt, 2H), 8.07 (dd, 1H), 8.25 (dd, 1H); pyridine protons, δ 6.95 (m, 2H, $H^{5'}_{py}$, $H^{3'}_{py}$, $J_{5'-3'}$ = 1.88 Hz), 7.38 (td, 1H, $H^{4'}_{py}$, $J_{4'-5'} = J_{4'-3'}$ = 7.60 Hz), 7.96 (d, 1H, $H^{6'}_{py}$, $J_{5'-6'}$ = 5.75 Hz); phenyl protons, δ 7.36, 7.68 (AB system, H^c, H^b, 4H); quinoline protons, δ 7.43 (dd, 1H, H^3_{qui}, J_{3-2} = 4.71 Hz), 7.31 (t, 1H, H^6_{qui}, J_{6-7} = 7.85 Hz), 7.11 (dd, 1H, H^7_{qui}, J_{7-5} = 1.32 Hz), 8.05 (dd, 1H, H^4_{qui}, J_{4-3} = 8.29 Hz), 7.70 (dd, 1H, H^5_{qui}, J_{5-6} = 7.85 Hz), 8.56 (dd, 1H, H^2_{qy}, J_{2-4} = 1.5 Hz). ^{13}C NMR ($CDCl_3$, T = 298 K, ppm): methyl carbon, δ 21.56 ($-CH_3$), aminomethyl carbon, δ 56.90 (pyr CH_2N); olefin carbons, δ 59.45, 60.98 (C=C), pyridine carbons, δ 124.21 ($C^{3'}_{py}$, $C^{5'}_{py}$), 136.92 ($C^{4'}_{py}$), 152.27 ($C^{6'}_{py}$), 153.99

(20) Newkome, G. R.; Gupta, V. K.; Fronczek, F. R.; Pappalardo, S. *Inorg. Chem.* **1984**, *23*, 2400.

($C^{2'}_{py}$); quinoline carbons, δ 122.97 (C^{3}_{qui}), 125.81 (C^{6}_{qui}), 130.08 (C^{5}_{qui}), 133.15 (C^{8a}_{qui}), 134.63 (C^{8}_{qui}), 136.92 (C^{4}_{qui}), 145.58 (C^{4a}_{qui}), 153.45 (C^{2}_{qui}); phenyl carbons, δ 128.78 (C^{c}_{ph}), 129.56 (C^{b}_{ph}), 129.81 (C^{a}_{ph}), 144.47 (C^{d}_{ph}); naphthoquinone carbons, δ 124.50, 124.62, 130.83, 130.95, 136.70; carbonyl carbons, δ 178.94, 180.06 (*C*=O). Anal. Calcd for $C_{32}H_{25}N_3O_4PdS$: C, 58.76; H, 3.85; N, 6.42. Found: C, 58.66; H, 3.81; N, 6.38.

[Pd(η^2-Nq)(NNNtos(Py))]. Yield: 91% (red microcrystals). IR (KBr pellet): ν_{C-H} 3072.0, 3026.0, 2927.2, $\nu_{C=O}$ 1624.1, 1584.6 cm^{-1}. ^1H NMR (CD_2Cl_2, T = 298 K, ppm): methyl protons, δ 2.53 (bs, 3H, $-CH_3$); olefin protons, δ 4.60 (bs, 2H, C=C$H_{naphtho}$); aminomethyl protons, δ 4.73 (bs, 4H, pyr- CH_2N); pyridine protons, δ 7.18 (t, 2H, H^5_{pyr}, J_{5-6} = 6.12 Hz), 7.52, 7.50 (m, 4H, H^3_{pyr}, $H^{Ar}_{naphtho}$), 7.65 (td, 2H, H^4_{pyr}, $J_{4-3} = J_{4-5}$ = 7.72 Hz, J_{4-6} = 1.51 Hz), 8.24 (bs, 2H, H^6_{pyr}); phenyl protons, δ 7.43, 7.65 (AB system, 4H, H^c, H^b); aromatic naphthoquinone protons, δ 8.02 (bs, 2H, $H^{Ar}_{naphtho}$). ^1H NMR ($CDCl_3$, T = 223 K, ppm): methyl protons, δ 2.52 (s, 3H, $-CH_3$, M), 2.64 (s, 3H, $-CH_3$, m); aminomethyl protons, δ 4.86, 4.94 (AB system, 4H, pyr CH_2N, J = 14.9 Hz, M), 4.03, 4.64 (AB system, 4H, pyr CH_2N, J = 14.8 Hz, m); olefin protons, δ 4.64 (s, 2H, C=C$H_{naphtho}$, M), 4.65 (s, 2H, C=C$H_{naphtho}$, m); pyridine protons, δ 7.99 (d, 2H, H^6_{pyr}, J_{6-5} = 5.1 Hz, M), 8.60 (d, 2H, H^6_{pyr}, J_{6-5} = 5 Hz, m); aromatic system, δ 7−8.25. Anal. Calcd for $C_{29}H_{25}N_3O_4PdS$: C, 56.36; H, 4.08; N, 6.80. Found: C, 56.40; H, 4.02; N, 6.78.

[Pd(η^2-Nq)(MeNS*t*-Bu)]. Yield: 94% (red microcrystals). IR (KBr pellet): ν_{C-H} 3006.2, 2953.6, 2841.7, $\nu_{C=O}$ 1624.1, 1584.6 cm^{-1}, $\nu_{C=N}$ 1604.4 cm^{-1}. ^1H NMR ($CDCl_3$, T = 298 K, ppm): *tert*-butyl protons, δ 1.31 (s, 9H, $-(CH_3)_3$); methyl protons, δ 2.80 (s, 3H, $-CH_3$); thiomethyl protons, δ 4.06 (s, 2H, pyr CH_2S); olefinic protons, δ 4.81 (AB system, *H*C=C$H_{naphtho}$); pyridine protons, δ 7.17 (m, 2H, H^3_{py}, H^5_{py}), 7.58 (t, 1H, H^4_{py}, J = 7.63 Hz); naphthoquinone protons, δ 7.51, 8.03 (m, 4H, $H^{Ar}_{naphtho}$). ^{13}C NMR ($CDCl_3$, T = 298 K, ppm): methyl carbon, δ 28.15 ($-CH_3$); *tert*-butyl carbons, δ 30.07 ($-C(CH_3)_3$); thiomethyl carbons, δ 39.53 (pyr *C*H_2S); quaternary *tert*-butyl carbons, δ 48.13 ($-C(CH_3)_3$); olefin carbons, δ 58.55, 62.37 (*C*=$C_{naphtho}$); pyridine carbons, δ 119.83 (C^3_{py}), 123.39 (C^5_{py}), 128.86 (C^6_{py}), 137.76 (C^4_{py}), 143.21 (C^2_{py}); naphthoquinone carbons, δ 125.23, 131.25 ($C^{Ar}_{naphtho}$), 135.84 ($C^{quat}_{naphtho}$), carbonyl carbons, δ 157.89, 162.17 (*C*=$O_{naphtho}$). Anal. Calcd for $C_{21}H_{21}NO_2PdS$: C, 54.84; H, 5.04; N, 3.05. Found: C, 54.88; H, 4.98; N, 3.11.

Synthesis of the Palladacyclopentadienyl Derivatives. The synthesis of the complexes [PdC_4(COOMe)$_4$(SNS(Me))] and [PdC_4(COOMe)$_4$(SNS(Ph))] was carried out according to published procedures.[4]

[PdC_4(COOMe)$_4$(NSN(Py))]. To 0.0706 g (0.327 mmol) of the ligand NSN(Py) dissolved in 12 mL of anhydrous acetone was added 0.1065 g (0.273 mmol) of $[PdC_4(COOMe)_4]_n$ under an inert atmosphere. The resulting solution was stirred for 2 h at room temperature and concentrated under vacuum. Addition of diethyl ether (20 mL) yields 0.1197 g (0.197 mmol) of the title substrate as yellow microcrystals. The complex was filtered off, washed with diethyl ether, and dried in a desiccator. Yield: 72%.

IR (KBr pellet): ν_{C-H} 2993.1, 2953.6, 2835.1, $\nu_{C=O}$ 1703.1, $\nu_{C=N}$ 1611.0 cm^{-1}. ^1H NMR ($CDCl_3$, T = 298 K, ppm): methyl ester protons, δ 3.07, 3.64 (s, 12H, $-COOCH_3$); thiomethyl protons, δ 4.18, 5.28 (AB system, 2H, pyr CH_2S); pyridine protons, δ 7.21 (m, 1H, H^3_{py}, H^5_{py}), 7.66 (t, 1H, H^4_{py}, $J_{4-5} = J_{4-3}$ = 7.63 Hz), 8.57 (m, 1H, H^6_{py}, J_{6-5} = 5.47 Hz). ^{13}C NMR ($CDCl_3$, T = 298 K, ppm): thiomethyl carbon, δ 43.37 (pyr *C*H_2S); methyl ester carbons, δ 50.23 ($-COOC^{\alpha}H_3$), 51.18 ($-COOC^{\beta}H_3$); pyridine carbons, δ 123.27 (C^5_{py}), 124.64 (C^3_{py}), 138.61 (C^4_{py}), 150.00 (C^6_{py}), 162.23 (C^2_{py}); cyclobutadienyl carbons, δ 163.81 (*C*=C), carbonyl carbons, δ 163.88 ($-C^{\beta}OOCH_3$), 172.62 ($-C^{\alpha}OOCH_3$). Anal. Calcd for $C_{24}H_{24}N_2O_8PdS$: C, 47.49; H, 3.99; N, 4.62. Found: C, 47.51; H, 4.03; N, 4.52.

The following complexes were synthesized in an analogous way using the appropriate ligands.

[PdC_4(COOMe)$_4$(NSN(Qui))]. Yield: 75% (yellow microcrystals). IR (KBr pellet): ν_{C-H} 3078.6, 2999.6, 2953.6, 2841.7, $\nu_{C=O}$ 1709.7, $\nu_{C=N}$ 1604.4 cm^{-1}. ^1H NMR (CD_2Cl_2, T = 298 K, ppm): methyl ester protons, δ 3.11, 3.63 (s, 12H, $-COOCH_3$); thiomethyl protons, δ 4.53 (s, 2H, pyr CH_2S), pyridine protons, δ 7.05 (t, 1H, $H^{5'}_{py}$, $J_{5'-6'}$ = 6.59 Hz), 7.13 (d, 1H, $H^{3'}_{py}$, $J_{3'-4'}$ = 6.59 Hz), 7.50 (td, 1H, $H^{4'}_{py}$, $J_{4'-5'}$ = 6.59 Hz, $J_{4'-6'}$ = 1.50 Hz), 8.70 (d, 1H, $H^{6'}_{py}$, $J_{6'-5'}$ = 6.59 Hz); quinoline protons, δ 7.55 (dd, 1H, H^3_{qui}, J_{3-2} = 4.81 Hz), 7.63 (t, 1H, H^6_{qui}, J_{6-7} = 7.80 Hz), 7.92 (d, 1H, H^5_{qui}, J_{5-7} = 1.23 Hz), 8.29 (dd, 1H, H^4_{qui}, J_{4-3} = 8.34 Hz), 8.37 (dd, 1H, H^7_{qui}, J_{5-6} = 7.80 Hz), 9.43 (dd, 1H, H^2_{qui}, J_{2-4} = 1.46 Hz). ^{13}C NMR (CD_2Cl_2, T = 298 K, ppm): thiomethyl carbon, δ 45.80 (pyr *C*H_2S), methyl carbons, δ 50.09, 50.88 ($-COOCH_3$); pyridine carbons, δ 122.93 ($C^{5'}_{py}$), 124.99 ($C^{3'}_{py}$), 137.57 ($C^{4'}_{py}$), 151.96 ($C^{6'}_{py}$), 156.75 ($C^{2'}_{py}$); quinoline carbons, δ 122.08 (C^3_{qui}), 127.53 (C^6_{qui}), 129.60 (C^{4a}_{qui}), 129.75 (C^8_{qui}), 131.20 (C^5_{qui}), 138.82 (C^4_{qui}), 140.97 (C^7_{qui}), 147.46 (C^{8a}_{qui}), 154.89 (C^2_{qui}); carbonyl carbons, δ 164.01, 173.29 ($-COOCH_3$); cyclobutadienyl carbons, δ 141.06, 165.72 (C^{α}=C, C^{β}=C). Anal. Calcd for $C_{27}H_{24}N_2O_8PdS$: C, 50.44; H, 3.76; N, 4.36. Found: C, 50.41; H, 3.69; N, 4.31.

[PdC_4(COOMe)$_4$(NNNtos(Py))]. Yield: 98% (yellow microcrystals). IR (KBr pellet): ν_{C-H} 2993.1, 2953.6, 2841.7, $\nu_{C=O}$ 1716.3, $\nu_{C=N}$ 1611.0 cm^{-1}. ^1H NMR (CD_2Cl_2, T = 298 K, ppm): methyl protons, δ 2.52 (s, 3H, $-CH_3$); methyl ester protons, δ 3.07, 3.62 (s, 12H, $-COOCH_3$); aminomethyl protons, δ 5.05, 5.35 (AB system, 2H, pyr CH_2N); pyridine protons, δ 7.30 (ddd, 1H, H^5_{py}, J_{5-4} = 6.37 Hz, J_{5-3} = 2.26 Hz), 7.75 (m, 2H, H^3_{py}, H^4_{py}), 8.61 (d, 1H, H^6_{py}, J_{6-5} = 5.34 Hz); phenyl protons, δ 7.45, 7.83 (AB system, H^c, H^d, 4H). ^{13}C NMR (CD_2Cl_2, T = 298 K, ppm): methyl carbon, δ 21.52 ($-CH_3$); methyl ester carbons, δ 50.29, 51.18 ($-COOCH_3$); aminomethyl carbon, δ 58.94 (pyr *C*H_2N); pyridine carbons, δ 124.23 (C^5_{py}), 126.8 (C^3_{py}), 138.74 (C^4_{py}), 150.04 (C^6_{py}), 158.15 (C^2_{py}); phenyl carbons, δ 126.8 (C^b_{ph}), 130.30 (C^c_{ph}), 135.66 (C^d_{ph}), 144.56 (C^a_{ph}); carbonyl carbons, δ 143.01, 163.58, 163.70, 172.62 ($-COOCH_3$). Anal. Calcd for $C_{31}H_{31}N_3O_{10}PdS$: C, 50.04; H, 4.20; N, 5.65. Found: C, 50.08; H, 4.23; N, 5.61.

[PdC_4(COOMe)$_4$(NNNtos(Qui))]. Yield: 92% (yellow microcrystals). IR (KBr pellet): ν_{C-H} 3078.6, 2993.1, 2953.6, 2841.7, $\nu_{C=O}$ 1709.7, $\nu_{C=N}$ 1604.4 cm^{-1}. ^1H NMR ($CDCl_3$, T = 298 K, ppm): methyl protons, δ 2.41 (s, 3H, $-CH_3$); methyl ester protons, δ 2.89, 3.35, 3.63, 3.78 (s, 12H, $-COOCH_3$); aminomethyl protons, δ 4.64, 5.28 (AB system, 2H, pyr CH_2N); pyridine protons, δ 6.97 (t, 1H, $H^{5'}_{py}$, $J_{5'-6'}$ = 6.22 Hz), 7.06 (d, 1H, $H^{3'}_{py}$, $J_{3'-4'}$ = 7.80 Hz), 7.46 (t, 1H, $H^{4'}_{py}$, $J_{4'-5'}$ = 6.97 Hz), 8.46 (d, 1H, $H^{6'}_{py}$); phenyl protons, δ 7.45, 8.46 (AB system, H^c, H^b, 4H); quinoline protons, δ 7.52 (dd, 1H, H^3_{qui}, J_{3-2} = 4.92 Hz), 7.62 (t, 1H, H^6_{qui}, J_{6-7} = 7.88 Hz), 7.83 (dd, 1H, H^7_{qui}, J_{7-5} = 1.32 Hz), 8.21 (dd, 1H, H^4_{qui}, J_{4-3} = 8.39 Hz), 8.34 (dd, 1H, H^5_{qui}, J_{5-6} = 7.88 Hz), 9.46 (dd, 1H, H^2_{qui}, J_{2-4} = 1.6 Hz). ^{13}C NMR ($CDCl_3$, T = 298 K, ppm): methyl carbon, δ 21.56 ($-CH_3$); aminomethyl carbon, δ 58.51 (pyr *C*H_2N); methyl carbons, δ 48.82, 50.69, 50.95, 51.21 ($-COOCH_3$); pyridine carbons, δ 123.38 ($C^{5'}_{py}$), 125.12 ($C^{3'}_{py}$), 138.09 ($C^{4'}_{py}$), 151.39 ($C^{6'}_{py}$), 154.84 ($C^{2'}_{py}$); quinoline carbons, δ 122.06 (C^3_{qui}), 127.17 (C^6_{qui}), 130.55 (C^5_{qui}), 131.41 (C^7_{qui}), 134.61 (C^8_{qui}), 138.74 (C^4_{qui}), 144.60 (C^{4a}_{qui}), 154.47 (C^2_{qui}); phenyl carbons, δ 129.85 (C^c_{ph}), 130.69 (C^b_{ph}), 131.69 (C^a_{ph}), 145.85 (C^d_{ph}); cyclobutadienyl carbons, δ 141.16, 143.55, 163.37, 167.43 (*C*=C); carbonyl carbons, δ 163.54, 165.00, 172.75, 173.34 ($-COOCH_3$). Anal. Calcd for $C_{34}H_{31}N_3O_8PdS$: C, 52.35; H, 4.01; N, 5.39. Found: C, 52.31; H, 3.95; N, 5.33.

X-ray Diffraction Analysis. For complexes **1** ([Pd(NNNtos(Qui))(η^2-tmetc)]), **2** ([Pd(NNNtos(Py))(η^2-tmetc)]), **3** ([Pd(NNNtos(Qui))(η^2-Nq)]), and **4** ([Pd(NSN (Qui))(η^2-tmetc)]), single crystals,

suitable for X-ray analysis, were obtained by slow precipitation from a CH_2Cl_2/*n*-hexane mixture. The intensity data were collected at room temperature, following the standard procedures. Two different instruments were used: a Philips PW1100 diffractometer (FEBO system) for complexes **1** and **2** and a STADI4 CCD diffractometer for complexes **3** and **4**. Both instruments were equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). All intensities were corrected for Lorentz−polarization and absorption effects.[21]

The structures were solved[22] by the heavy-atom method for complexes **1** and **2** and by direct methods for complexes **3** and **4**. The refinements[23] were carried out for all structures by full-matrix least-squares procedures based on F_o^2, using anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were placed in calculated positions with fixed, isotropic thermal parameters. The calculations were performed with the SHELXTL package. Crystallographic and experimental details for the structures are summarized in the Supporting Information, while Table 1 gives selected bond distances and angles.

Supporting Information Available: Text giving equilibrium and rate constant determination and calculation details, CIF files giving X-ray crystallographic data in CIF format, and a table giving a summary of crystal data and refinement details. This material is available free of charge via the Internet at http://pubs.acs.org.

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